

Characterization of Block Copolymers Synthesized via Transition Metal Mediated Living Radical Polymerization

Application Note

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Introduction

Polymerization reactions mediated by the presence of a transition metal have received much interest in both literature and the commercial world. These processes allow the controlled synthesis of polymers of predetermined molecular weight, polydispersity and well-defined architecture using cheap and synthetically simple procedures. Generation of a carbon radical initiates free-radical polymerization in the presence of a monomer and a suitable solvent. Termination steps are minimized by the reversible nature of the radical formation reaction. Careful tailoring of the relative reaction rates can lead to well-controlled polymerizations where termination steps are sufficiently controlled to allow polymers of polydispersity of 1.1 to be produced from the reaction. These reactions typically follow pseudo-first order kinetics. The ability to readily convert hydroxyl functional groups to active initiator groups ready for polymerization leads to a convenient synthetic pathway for the synthesis of architecturally diverse materials such as stars, blocks and grafts.

One such class of polymer structures that may be prepared using this synthetic process are block copolymers. These copolymers are made up of two or more chains that contain different repeat units that are known as blocks, for example a block of polystyrene connected to a block of polymethyl methacrylate repeat units. The materials are of interest because under certain conditions they facilitate phase separation, forming nanostructures with properties that differ from the equivalent blended material or from random copolymers of the monomers used in the two blocks.

Determining the molecular weight of block copolymers is not straightforward as the composition of the material affects the molecular dimensions, which in turn means that molecular weights determined by conventional GPC using only a refractive index detector are inaccurate. However, using viscometry, it is possible to determine the molecular weights of these materials by the universal calibration approach.



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This methodology makes use of the relationship between molecular weight and molecular density, allowing accurate molecular weights to be determined for materials irrespective of their chemistry. This note describes the analysis of a series of five poly(styrene-co-methyl methacrylate) copolymers manufactured with different molecular weights by GPC viscometry.

Results and Discussion

Conditions

Columns: 2 x Agilent PLgel 5 μ m MIXED-C, 300 x 7.5 mm (part number PL1110-6500)
 Eluent: Tetrahydrofuran
 Flow Rate: 1 mL/min
 Inj. Vol: 100 μ L
 Sample Conc: 2 mg/mL
 Temp: 40 °C
 Detectors: Agilent 390-MDS Multi Detection Suite comprising a differential refractive index and a four capillary bridge viscometer
 Calibration Standards: Agilent Polystyrene EasiVials

Figure 1 shows overlaid dual detector raw data chromatograms for a poly(styrene-co-methyl methacrylate) sample showing the data collected from the individual detectors. The polymers all eluted as narrow near-Gaussian peaks.

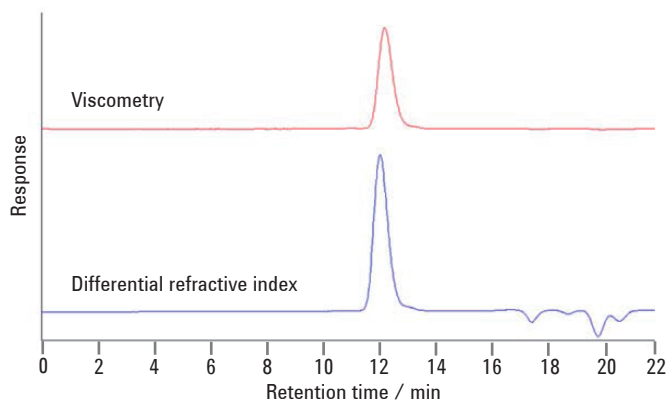


Figure 1. Overlaid dual detector raw data chromatograms for a block copolymer sample

The samples were all then analyzed by GPC with viscometry, employing the universal calibration method to determine molecular weights that were not dependent on calibrant chemistry. The overlaid molecular weight distributions are shown in Figure 2.

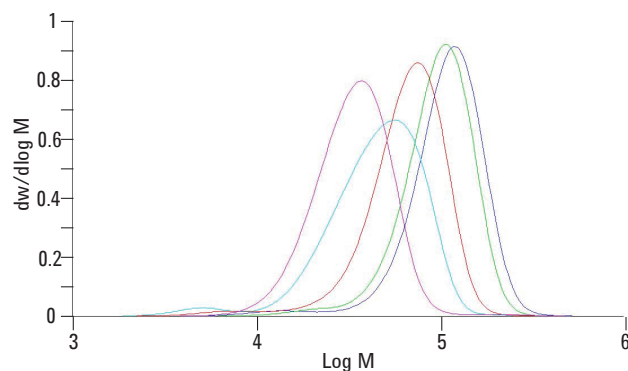


Figure 2. Overlaid molecular weight distributions calculated by universal calibration analysis of all samples

The Mark-Houwink plots for the four materials are shown in Figure 3.

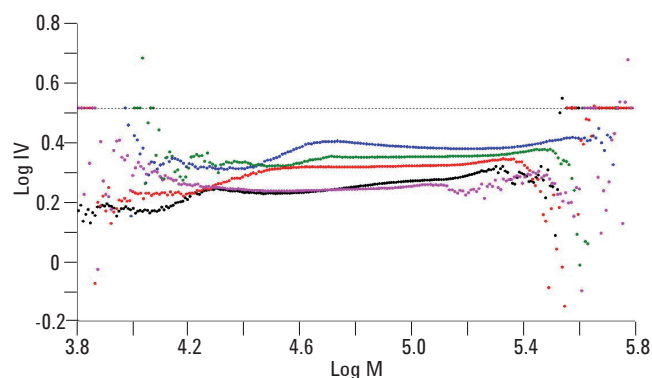


Figure 3. Overlaid molecular weight distributions calculated by universal calibration analysis of all samples

The Mark-Houwink relationship describes the scaling behavior of the intrinsic viscosity of polymers as a function of molecular weight. Assuming that materials have the same molecular density, they will follow the same Mark-Houwink plot. In these samples the variations in the block lengths for the different samples have caused shifts in the Mark-Houwink plots.

Conclusion

The 390-MDS multi detection suite successfully determined the molecular weights of some block copolymers and revealed differences in the block lengths. Viscometry detection delivered by the 390-MDS is a powerful tool for investigating the molecular weight and structural properties of polymers, irrespective of their chemistry.

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